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Title: HIGH PRESSURE METALLIZATION AND AMORPHIZATION OF THE MOLECULAR CRYSTAL $SN(IBr)_2$

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High pressure metallization and amorphization of the molecular crystal $Sn(IBr)_2$.

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ABSTRACT

An insulator-to-metal transition concurring with amorphization is found in the cubic ($Pa\bar{3}$) molecular crystal $Sn(IBr)_2$ at $P \approx 20$ GPa. Measurements were carried out with diamond-anvil cells at pressures up to ~30 GPa using resistance measurements, X-ray diffraction (XRD), and ^{119}Sn Mössbauer spectroscopy (MS). With increasing pressure a new crystalline phase is observed in the 10 -23 GPa range; at $P \approx 16$ GPa a gradual onset of structural disorder is first observed, and full amorphization takes place at $P \geq 21$ GPa. Both electronic proprieties as measured by R(P,T) and MS data are consistent with a gradual growth of disordered $(SnI_2Br_2)_n$ polymeric chains, formed by intermolecular I - I bonding allowing for electronic delocalization to occur. Upon decompression both XRD and ^{119}Sn MS show a significant pressure hysteresis.

Keywords: insulator-metal transition, pressure-induced amorphization, pentatomic molecular crystals.

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INTRODUCTION

The concurrence of pressure-induced (PI) *amorphization* and *insulator-metal* (IM) transition in the pentatomic molecular crystals GeI_4 and SnI_4 had been the subject of various studies [1,2,3]. However in the case of the $SnBr_4$ molecular crystal, both optical [4] and ^{119}Sn Mössbauer studies [5] definitely showed that this phenomenon does not occur; to P > 25 GPa the bromide which becomes amorphous at ~12 GPa, remains a large-gap insulator. From this it was concluded [5] that the mechanism for amorphization in the iodides must be of a different nature; the enhanced *intermolecular* I - I overlap at high pressure proposed as the mechanism for the onset of both *structural disorder* and *gap closure* [1,2] may not take place in $SnBr_4$. To test the proposed mechanism, we carried out X-ray diffraction (XRD), resistance measurements, R(P,T), and Mössbauer spectroscopy (MS) measurements of the mixed-halides molecular crystal $Sn(IBr)_2$ to pressures of ~30 GPa using diamond anvil cells. As will be shown, the combination of these methods provide unique information about the crystalline and disordered metallic states.

EXPERIMENTAL

Polycrystalline and single crystal samples of $Sn(IBr)_2$ were synthesized by direct vapor-solid reaction of spectroscopical pure IBr and Sn metal in an evacuated glass tube at 230 °C. At ambient pressure $Sn(IBr)_2$ is an orange-red crystal whose structure was unknown. Its structure was determined using single-crystal XRD studies and was found to be cubic (space group $Pa\bar{3}$), with eight molecules per unit cell, and lattice parameter: a = 12.022(1) Å. The structure is identical to that of SnI_4 but with a-value smaller by about 0.250 Å. Details about ambient pressure structure of $Sn(IBr)_2$ will be published elsewhere.

TAU diamond anvil cells (DACs) of the miniature type [6], with anvil culets in the 0.4 - 0.5 mm range were used in conjunction with ruby fluorescence for manometry. Powder XRD was carried out at CHESS using the energy dispersive mode, and data were collected at 300 K with $2\theta = 8°$. Resistance measurements were carried out using the four- probe method in the 5 - 300 K temperature range. For the Mössbauer experiments a

5 mCi $Ca^{119m}SnO_3$ commercial source was used and measurements were carried out at 75 K.

RESULTS AND DISCUSSION

With pressure increase a new crystalline phase was detected at ~10 GPa and having an unknown structure. This phase coexists with the original low pressure phase in the range 10-21 GPa. It is noteworthy that at ~ 8 GPa a structural phase transition was also observed in the isostructural SnI_4 [7]. At $P \approx 16$ GPa a broad diffraction peak typical of a diffraction halo in glasses starts to appear. The relative intensity of this halo increases with pressure, and at $P \geq 23$ GPa no remnants of crystalline phases are observed. Upon decompression the original crystalline phase reappears between 4.7 and 0.15 GPa, coexisting with remnants of the amorphous phase (see Fig. 1).

The onset of the metallic state is determined from R(P,T) measurements. Figure 2 shows the resistance variation with temperature for several pressures close to the IM transition. The metallic state is determined by the change in sign of dR/dT, from negative to positive. And indeed the first R(T) curve showing a positive slope at $T > 65$ K is found for P = 22.7 GPa, and at P = 24 GPa metallization takes place in the full 5 - 300 K temperature range. The inset in Fig.2 shows the resistance variation with pressure at 300 K. Definite change in the R(P) slope is observed at ~11 GPa, probably related to the crystallographic phase transition as observed with XRD. At ~ 20 GPa the slope is further reduced, coinciding with the onset of an IM transition.

Representative Mossbauer spectra of $^{119}Sn(IBr)_2$ at various pressures during compression are shown in Fig.3. The spectra obtained in the 0 -8 GPa range show a single line with an isomer shift (IS) of about 1.6 mm/sec relative to $CaSnO_3$ (Fig 3a). This value of IS is typical of covalently bound four-coordinated Sn^{4+} [8]. Despite the mixed halides forming the pentatomic molecule, the lack of a detectable quadrupole splitting suggests a rather symmetric tetrahedron. At $P \geq 8$ GPa a second unsplit component with IS = 3.9 mm/sec appears (Fig. 3b). We suppose that this large value of IS is due to the onset of a six-fold coordination and is attributed to a new configuration of 5s5p-4p4d hybridization, which results in an increase of the 5s electron density.

The pressure dependence of the relative abundance of the amorphous phase is shown in Fig.4. This was obtained from the relative area under the absorption peaks of the MS spectra. The pressure hysteresis is clearly observed, which qualitatively agrees with the XRD data.

CONCLUSIONS

The present results with the mixed halide $Sn(IBr)_2$ molecular crystal confirms the model proposed by Pasternak, Taylor, and co-workers in their studies of SnI_4 and GeI_4 [1,3], namely, the high pressure phase with its six-coordinated Sn^{4+} is in the form of a structurally disordered polymeric $(Sn(IHa)_2)_n$ (Ha = Br, I) clusters. This structure could be formed due to the enhanced intermolecular I-I overlap. For each molecule, two iodides serve as bridging atoms to form the intermolecular chain. This polymerization process can account for the metallic behavior of $Sn(IBr)_2$ by providing a pathway of electron delocalization along the -Sn-I-I-Sn- linkage of the chains. The cluster's size increases with pressure culminating into a full concurrent amorphous and metallic phase. It is noteworthy that in analogous SnI_4 the metallization onset appears at approximately the same pressure of 19.8 GPa [2]. The amorphization process of the iodide and halide-mixed pentatomic crystals is in contrast to that of the tin bromide case [5] where at ~9 GPa $(SnBr_4)_2$ dimers are formed, an amorphous phase is created, yet, the material remains a *bona-fide* insulator to pressures above 25 GPa.

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[9] The closure of the Sn^{4+} intra 5s5p-4p4d gap could be the reason for the intra-molecular electron delocalization which by virtue of I-I intermolecular bridging results in the pressure-induced metallization.

Figures captions:

Fig.1. X-ray diffraction patterns of the crystalline (a) and amorphous (b) phases of $Sn(IBr)_2$ upon compression. The upper part (c) shows the pattern of the crystalline phase following decompression. Indices of major reflections from the $Pa\bar{3}$ structure are given in (a) and (c). Peak letters denote the atomic excitations of I-K, I-$K_{\beta 1}$; Sn-K, Sn-$K_{\beta 1}$; Sn-$K_{\alpha 1}$, Sn-$K_{\alpha 2}$ edges.

Fig.2. Temperature dependence of the resistance of $Sn(IBr)_2$ for various pressure values close to the IM transition. Incipient metallic behavior is first observed at 22.7 GPa. The inset shows log(R) versus pressure recorded at 300 K. Note the changes in slope at ~ 12 GPa and ~20 GPa where a structural transition and an IM transition are observed, respectively.

Fig.3. Mössbauer spectra of $^{119}Sn(IBr)_2$ at 75 K with increasing pressure. Characteristic IS for the low pressure crystalline phase, where the tetravalent Sn is four-fold coordinated, is ~1.6 mm/s. The IS for the amorphous phase, where Sn is six-fold

coordinated, is ~3.9 mm/s. Values of IS are with respect to the calcium stannate source at the same T.. Solid lines are theoretical fits to the data.

Fig.4. The pressure dependence of the relative abundance of the high pressure amorphous phase as recorded by MS studies. The solid and open symbols correspond to abundance upon compression and decompression, respectively.

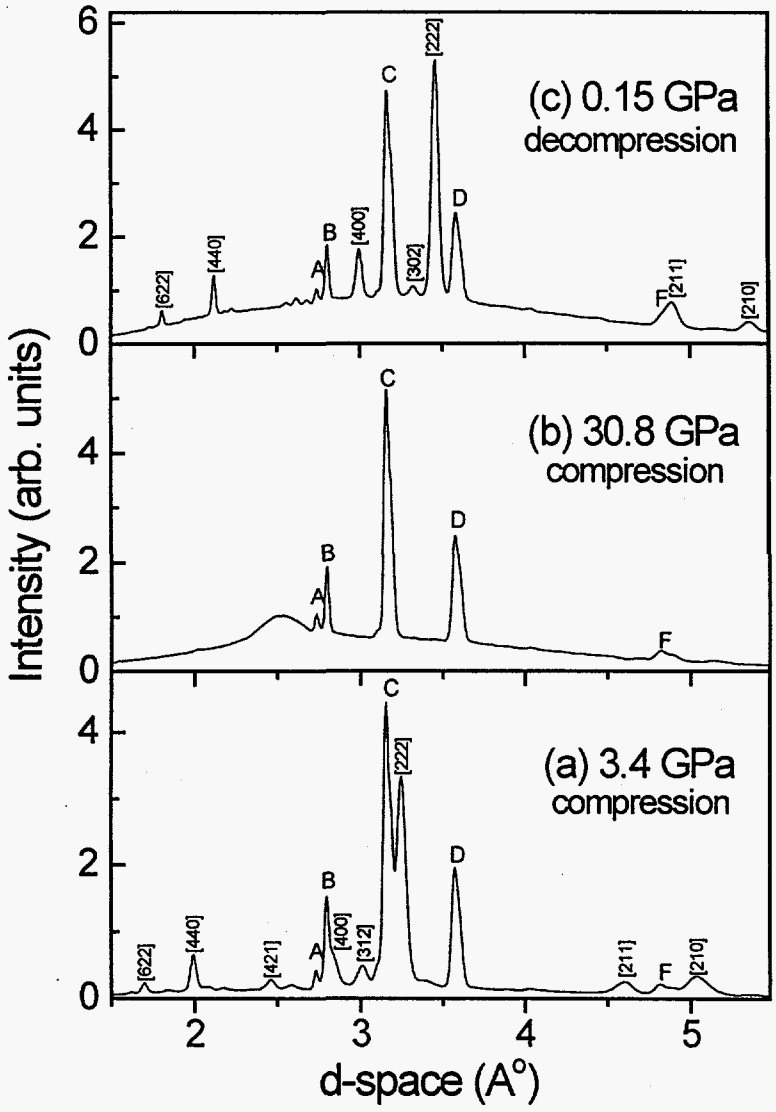
(c) 0.15 GPa
decompression
(b) 30.8 GPa
compression
(a) 3.4 GPa
compression
Intensity (arb. units)
d-space (A°)
[622]
[440]
[421]
[400]
[312]
[302]
[222]
[211]
[210]
A
B
C
D
F

Fig. 1

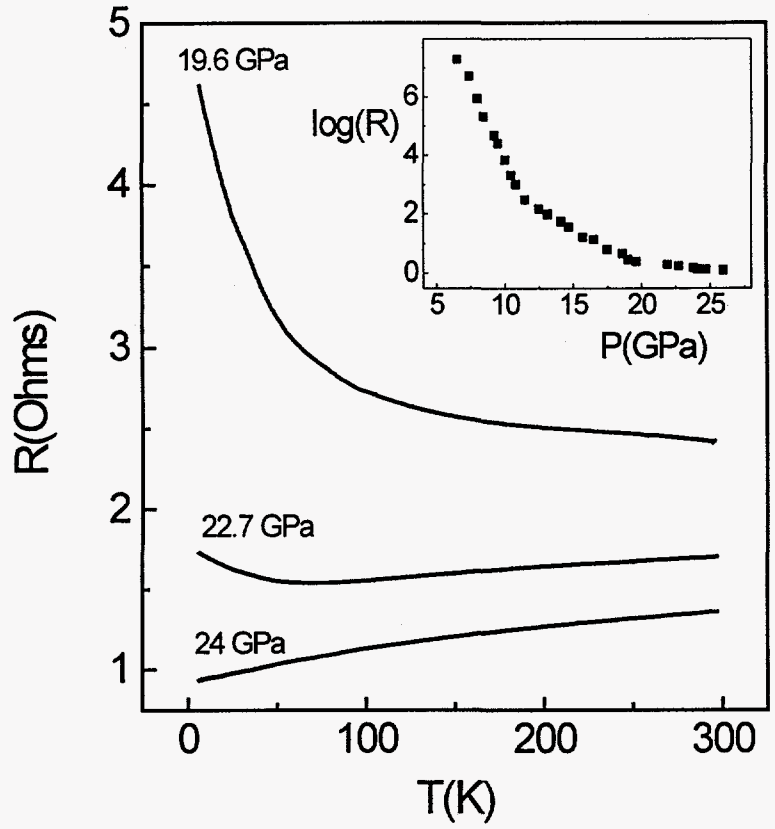

Fig. 2

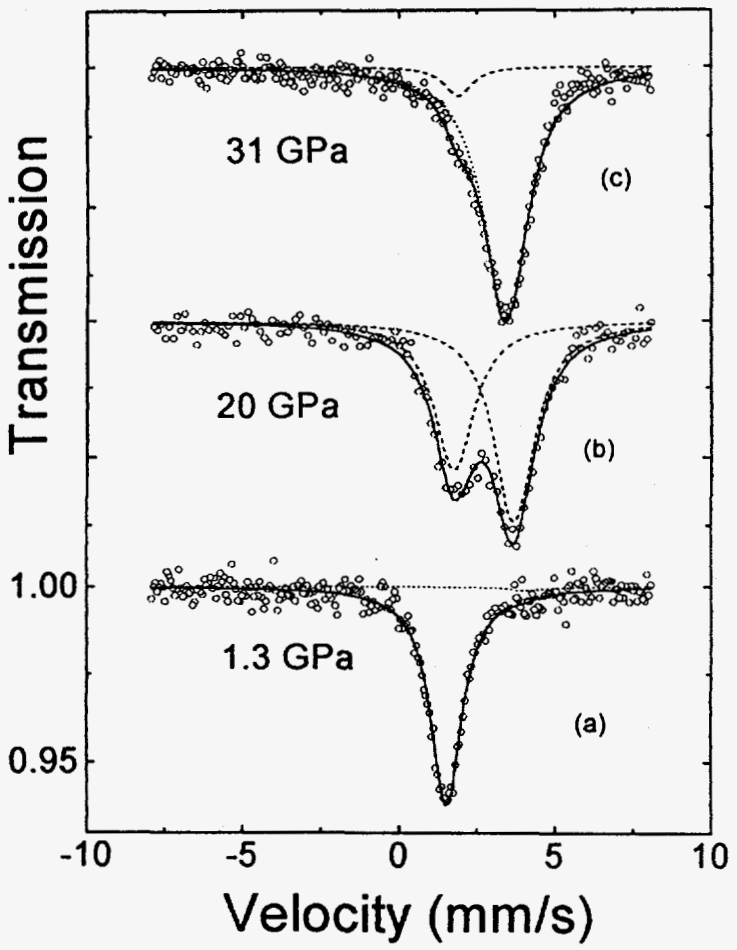
Transmission
31 GPa
(c)
20 GPa
(b)
1.3 GPa
(a)
1.00
0.95
-10
-5
0
5
10
Velocity (mm/s)

Fig. 3

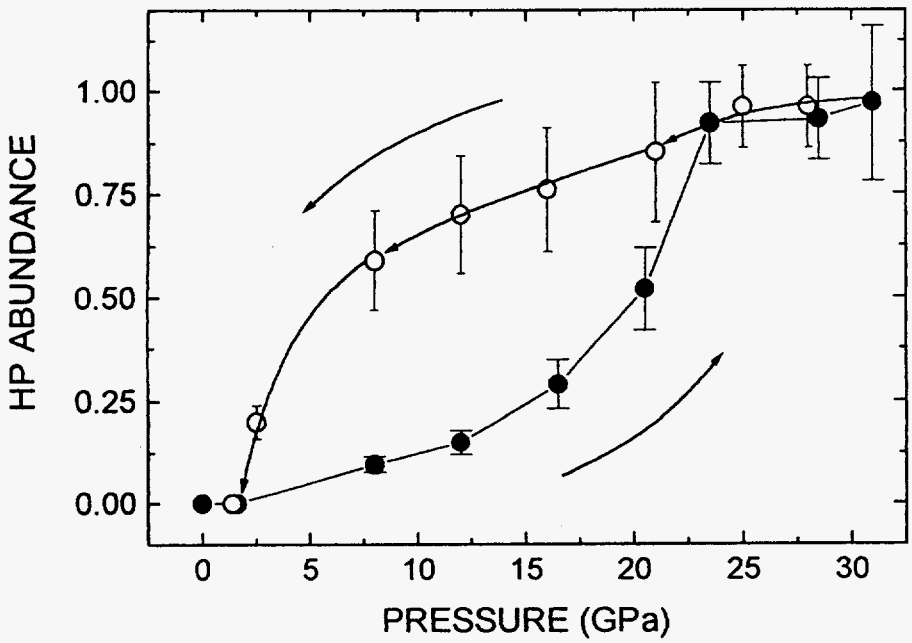

Fig. 4